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Media for ultrafast THz photonics

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Designing of the ultrafast terahertz photonics devices requires materials with the biggest nonlinear refractive index coefficient n_2 and the lowest nonlinear response settling time τ in the terahertz spectral range. In the present study, we show that the ratio n_2/τ for media with the vibrational nonlinearity in the terahertz range is determined by the square of the medium thermal expansion coefficient and the fifth power of its dominative stretching vibrational mode frequency. These findings are based on the theory of the media vibrational nature nonlinear polarization response to incident THz radiation. We provide estimated values of the n_2/τ ratio for a group of liquids and crystal materials. According to our evaluations, n_2/τ value for alpha-pinene in the terahertz spectral range is about 10^6 cm^2/J and is almost the biggest one compared to materials with different nonlinearity types in various spectral ranges.

Keywords: THz spectral range, high intensity radiation, strong field, vibrational nonlinearity, nonlinear refractive index coefficient, nonlinearity settling time.

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Introduction

At the moment, terahertz (THz) technology is one of the frontier photonics area, which is due to the relatively recent appearance of powerful sources of picosecond THz pulses [1]. Pulsed THz radiation has found wide application in various technological branches, such as biology, medicine and communication systems [2–4]. In particular, due to the fact that the nonlinear refractive index coefficient n_2 of a number of liquids and crystalline materials in the THz range was found to be low-inertia and orders of magnitude greater than in the visible and near-infrared (NIR) ranges [5–8], it became possible to create ultrafast THz photonics devices, whose action is based on the self-action effects of pulsed THz radiation in nonlinear media. For example, bistable interferometers well-known from applications in other spectral ranges [9–11] can be used in the THz range to create THz transistors and memory cells.

The theory describing the giant and low-inertia nonlinearity in the THz range was proposed in [12]. This theory is based on the hypothesis that anharmonic oscillations of atoms in molecules are the dominant nonlinearity mechanism in the THz spectral range. Experimental results of measuring the nonlinear refractive index for a number of liquids in the THz spectral range correlate well with the predictions provided by the theory of vibrational nonlinearity for these substances [5–8,13]. It is important to note that studies of nonlinearity in the THz range have been conducted for a small number of materials, selected in a non-systematic way due to the lack of clear criteria by which to predict the magnitude of n_2 value in certain media. At the same time, to create of ultrafast THz photonics devices, materials with the maximum value of the nonlinear refractive index coefficient are required. Thus, it is obvious that there is a need to search for such substances among the wide variety of media used in THz photonics. The search, in turn, implies clear criteria, which are not currently available.

Media suitable for the designing of ultrafast THz photonics devices must have not only a high value of the nonlinear refractive index coefficient, but also a small inertia of the nonlinearity mechanism, or, in other words, a small nonlinear response settling time [14]. It is experimentally confirmed that the inertia of the vibrational nonlinearity in the THz range does not exceed 1 ps [5]. It is this fact that makes the use of vibrational nonlinearity in the THz range unique and promising, since giant nonlinearity itself is also present in other areas of the spectrum. For example, in the IR range, a giant thermal nonlinearity (n_2 on the order of $10^{-3}-10^{-5}$ cm^2/W) is known, which due to its nature has a large inertia (on the order of $10^{-3}-10^{-1}$ s) [15]. Nevertheless, to select the most effective materials in terms of designing ultrafast THz photonics devices, the accuracy of experimental estimates for the inertia of the nonlinearity mechanism is not enough. An analytical model describing the dispersion inertia of vibrational nonlinearity, developed on the basis of the theory suggested in [12], was proposed by the authors of this publication in work [16]. However, it is known that the inertia of vibrational nonlinearity is caused not only by the radiation dispersion, but also by its absorption during propagation in matter, which was not taken into account in the work [16]. The publication [16] also did not provide a sufficient analysis of the physical phenomena that determine the value of the nonlinear response settling time. At the same time, apart from the publication [16], it is not known about the works devoted to the theoretical study of the vibrational nonlinearity inertia.

Due to the fact that the nonlinearity efficiency is mainly determined by its magnitude and settling time (which are characterized by the coefficient of nonlinear refractive index n_2 and inertia time constant of nonlinearity mechanism τ respectively), to evaluate the most promising materials in terms of their application in ultrafast THz photonics devices, it is reasonable to introduce and determine the parameter n_2/τ [14]. In the present work, we derive an analytical formula to calculate this ratio through the optical, thermal, and spectral matter properties available in the reference sources. The influence of various medium parameters on the value of this ratio is analyzed. The key of them are demonstrated. Estimates of n_2/τ are given for a number of common liquids and crystalline materials. It is demonstrated that the value of this ratio obtained for alpha-pinene in the THz range is maximum among all studied materials with different nonlinearity mechanisms in other spectral ranges.

Nonlinear refractive index coefficient of vibrational nature in the field of terahertz radiation

The dynamics of the vibrational polarization response $P = P_{\text{lin}} + P_{nl}$ (where P_{lin} and P_{nl} — its linear and nonlinear parts, respectively) of an isotropic dielectric medium in the field of linearly polarized THz radiation can be described by a system of parametrically interrelated scalar equations [16]

$$\begin{gathered}\frac{\partial^2 P_{\text{lin}}}{\partial t^2} + \gamma\frac{\partial P_{\text{lin}}}{\partial t} + \omega_0^2 P_{\text{lin}} = Nq\alpha E,\\ \frac{\partial^2 P_{nl}}{\partial t^2} + \gamma\frac{\partial P_{nl}}{\partial t} + \omega_0^2 P_{nl} = RP_{\text{lin}} - \frac{b}{(Nq)^2}P_{\text{lin}}^3, \qquad (1)\\ \frac{\partial^2 R}{\partial t^2} + \gamma\frac{\partial R}{\partial t} + \omega_0^2 R = \frac{2a^2}{(Nq)^2}P_{\text{lin}}^2,\end{gathered}$$

where E — electric field strength of THz pulse; t — time; γ — molecular oscillator damping coefficient; ω_0 — frequency of its free oscillations (identified with stretching vibrational bond central frequency from the fundamental absorption spectrum of matter); N — the number density of molecular oscillators in matter; q — effective charge of molecular oscillator; α — molecular polarizability; R — the functional describing the contribution of the quadratic anharmonic local molecular oscillations to the macroscopic cubic polarization response of the medium; b and a are the coefficients characterizing the cubic and quadratic anharmonicity of local molecular oscillations in the equation for the anharmonic molecular oscillator

$$\frac{\partial^2 x}{\partial t^2} + \gamma\frac{\partial x}{\partial t} + \omega_0^2 x + ax^2 + bx^3 = \alpha E,$$

where x — the atom deviation from its equilibrium position.

In the case of non-resonant interaction of matter with incident radiation, the system (1) satisfies the conditions

$$\omega_0^2 P_{\text{lin}} \gg \gamma\frac{\partial P_{\text{lin}}}{\partial t}, \frac{\partial^2 P_{\text{lin}}}{\partial t^2},$$

$$\omega_0^2 R \gg \gamma\frac{\partial R}{\partial t}, \frac{\partial^2 R}{\partial t^2},$$

allowing to apply the method of successive approximations to find the solution to (1). Using this approach, the solution to system (1) for the nonlinear cubic polarization response we obtain

$$\begin{aligned}P_{nl} = {}&\chi^{(3)}E^3 - \chi^{(3d)}\frac{\gamma}{\omega_0^2}E^2\frac{\partial E}{\partial t} - \chi^{(3d)}E\left(\frac{\partial E}{\partial t}\right)^2\\ &- \chi^{(3d)}\frac{1}{\omega_0^2}E^2\frac{\partial^2 E}{\partial t^2},\end{aligned} \qquad (2)$$

where

$$\chi^{(3)} = \frac{\chi_{\text{lin}}\alpha^2}{\omega_0^6}\left(\frac{2a^2}{\omega_0^2} - b\right) \qquad (3)$$

is the non-resonant cubic nonlinear susceptibility of vibrational nature;

$$\chi_{\text{lin}} = \frac{qN\alpha}{\omega_0^2} \qquad (4)$$

is the non-resonant linear susceptibility of vibrational nature;

$$\chi^{(3d)} = \frac{2\chi_{\text{lin}}\alpha^2}{\omega_0^6}\left(\frac{8a^2}{\omega_0^2} - 3b\right) \qquad (5)$$

is the first dispersion additive to the non-resonant nonlinear cubic susceptibility of vibrational nature.

In the CGS system, the nonlinear refractive index coefficient is related to the cubic nonlinear susceptibility through the ratio $n_2 = 3\pi\chi^{(3)}/n_0$, where n_0 is the linear refractive index [17]. In this case, the non-resonant nonlinear refractive index coefficient of vibrational nature is expressed by the formula

$$n_2 = \frac{3\pi\chi_{\text{lin}}\alpha^2}{n_0\omega_0^8}(2a^2 - b\omega_0^2). \qquad (6)$$

Obviously, depending on the ratio of the contributions $2a^2$ and $b\omega_0^2$ associated with the quadratic and cubic anharmonicity of molecular vibrations, respectively, expression (6) can be both positive and negative. In the paper [12], it is shown that in the THz range, the coefficients a and b are expressed through the thermal and optical properties of matter known from the reference literature using the ratios

$$a = -\frac{m\omega_0^4 a_1}{k_B}\alpha_T, \qquad (7)$$

$$b = \frac{6\pi q^2 N\omega_0}{(n_{0,\nu}^2 - 1)\hbar}, \qquad (8)$$

where m is the effective mass of the molecular oscillator, $n_{0,\nu}$ is the vibrational contribution to the linear refractive index of the medium in the case of $\omega \ll \omega_0$; $\hbar$ is the reduced Planck constant. From this, it is not difficult to obtain the ratio of these two contributions

$$2a^2/b\omega_0^2 = \frac{\hbar}{3\pi k_B^2}\frac{m^2}{q^2}\frac{a_1^2}{N}\omega_0^5\alpha_T^2(n_{0,\nu}-1). \qquad (9)$$

Formula (9) shows, it is clear that for media with high-frequency vibrational bonds, a large coefficient of thermal expansion, and a large vibrational contribution to the linear refractive index, the dominance of the quadratic anharmonicity of local molecular oscillations and, consequently, a positive nonlinear refractive index coefficient is expected. Conversely — when ω_0, α_T and $n_{0,\nu}$ are small, the cubic anharmonicity of local molecular vibrations is expected to dominate and the nonlinear refractive index coefficient of the medium is correspondingly negative. Table 1 shows the experimentally obtained and theoretically calculated via analytical formula (6) values of the nonlinear refractive index coefficient, as well as the values of the characteristic parameters ω_0, α_T and $n_{0,\nu}$ and ratio $2a^2/b\omega_0^2$ for some liquid and solid materials. The choice of these media is based on the following considerations. In liquid water (hereinafter — water), despite the strong absorption in the THz range, it is possible to generate nonlinear effects by using thin jets [5]. Moreover the nonlinear refractive index coefficient of water in the THz range is a million times greater than in the optical one [5–8]. Alpha-pinene has excellent transparency in the THz range (absorption coefficient less than $2\,\mathrm{cm}^{-1}$ [18]). Lithium niobate is currently one of the most versatile optical materials, so it is used in a wide spectral range —from near-UV to far-IR [19]. Finally, NaCl and KCl — are isotropic crystals with transparency in the range of 0.1–0.3 THz [20] and an alkaline halide structure that is best described by the anharmonic oscillator model [21].

The central frequencies of free oscillations ω_0 in the first column of Table 1 were determined by the dominant vibrational bonds in the absorption spectrum of the substances in question. The dominant bonds, in turn, were determined by approximating the linear refractive index data for the materials in the optical range using the Sellmeier equation [21]

$$n_0^2 = 1 + \sum_i \frac{A_i\lambda^2}{\lambda^2-\lambda_{el,i}^2} + \sum_i \frac{B_i\lambda^2}{\lambda^2-\lambda_{\nu,i}^2}, \qquad (10)$$

where λ — is the central wavelength of incident radiation; $\lambda_{el,i}$ and $\lambda_{\nu,i}$ — effective wavelengths characterizing the electronic and vibrational contributions to the linear refractive index at different frequencies, respectively; A_i and B_i — empirical constants characterizing the magnitude of the electronic and vibrational contributions to the linear refractive index at different frequencies, respectively. In particular, for water, the effective wavelength $\lambda_{\nu,i}$ corresponding to the maximum coefficient B_i is $3\,\mu$m (100 THz) [22]; at the same time, in the fundamental absorption spectrum of water, the dominant band corresponding to valence O–H vibrations is also centered at 100 THz [23]. Finally, using exactly this frequency in formula (6) allows us to obtain an analytical value of the nonlinear refractive index coefficient, which correlates perfectly with experiment [8]. The experimental data necessary to obtain formula (10) are available for all materials in Table 1 except α-pinene. Therefore, for this medium ω_0 was estimated only from the fundamental vibrational absorption spectrum [24].

The formula (10) allows us to estimate the linear refractive index with required accuracy in the optical range. However, in the THz range, it is not applicable due to the need to consider additional vibrational modes. Despite this, using (10) it is possible to estimate the electronic contribution n_{el} to the linear refractive index for THz frequencies and calculate the vibrational part of the linear refraction index in the THz range via the formula $n_{0,\nu} = \sqrt{1 + n_0^2 - n_{\mathrm{el}}^2}$ [12]. This is how the values in the fourth column of Table 1 have been obtained.

Table 1 shows that the greatest in the absolute value and positive in sign coefficient of nonlinear refractive index have liquids H_2O and α-pinene, which is due to the giant (by 4–6 orders) superiority in these media quadratic anharmonicity of molecular vibrations over the cubic ones. This fact, in turn, is related to the large coefficient of thermal expansion (that is typical for) and the high-frequency dominant vibrational bonds in liquids. The experimentally measured values of n_2 for water correlate perfectly with the theory; for alpha-pinene, there is a discrepancy of 1–2 orders of magnitude (depending on the experimental data), which for such a small value is not a significant deviation. Table 1 demonstrates that the nonlinear refractive index coefficient of liquids in the THz range is orders of magnitude greater than in the IR range.

Isotropic crystals NaCl and KCl have a negative sign and a relatively small the absolute value of n_2. Table 1 shows that the cubic anharmonicity of molecular oscillations slightly prevails in these materials. It is associated with a small coefficient of thermal expansion and low-frequency vibrational bonds (typical for crystals), as well as the isotropy of the molecular structure. Nothing is known about the experiments to measure n_2 for these media the THz range, so in this case it is not possible to compare the theoretical results with the experimental ones. Nevertheless, it is obvious that the the n_2 values for these materials in the THz range exceed similar values in the IR range insignificantly.

For the anisotropic $LiNbO_3$ crystal, the case of THz radiation propagation along direction X (coinciding with the direction *a* in the hexagonal lattice of lithium niobate [25]) has been considered, which is perpendicular to the direction of the optical axis C (aka — Z-axis), with ordinary (the electric field vector of the pulse lies in the plane perpendicular to the optical axis) and extraordinary (the electric field vector is parallel to the optical axis) polarization. In this direction, lithium niobate has a maximum linear coefficient of thermal expansion —almost 4 times greater than in the direction of the optical axis [26]. In contrast to isotropic crystals, $LiNbO_3$ has a noticably large n_2 (at least

Table 1. Nonlinear refraction index coefficient of vibrational nature and and matter properties determning its value for a number of solid and liquid optical materials at room temperature and normal pressure

Material	$\omega_0/2\pi$, THz	$10^4\alpha_T$, K^{-1}	$n_{0,\nu}$	$2a^2/b\omega_0^2$	$n_2, \mathrm{cm}^2/\mathrm{W}$		
					Theory , THz	Experiment	
						THz	IR
α-pinene $C_{10}H_{16}$	87.5 [24]	9.5 [27]	1.21	$1 \cdot 10^6$	$2 \cdot 10^{-8}$	$3 \cdot 10^{-9}$[8] $1.3 \cdot 10^{-10}$ [7]	$1.5 \cdot 10^{-15}$ [28]
H_2O	100 [22]	2.1 [29]	1.94	$2 \cdot 10^4$	$5 \cdot 10^{-10}$	$7 \cdot 10^{-10}$[5] $6.5 \pm 2.6 \cdot 10^{-10}$ [6] $7.8 \pm 3 \cdot 10^{-10}$ [7]	$1.9 \cdot 10^{-16}$[30]
$LiNbO_3$ (o-wave: $\mathbf{k}^* \parallel X$, $\mathbf{E} \perp Z$)	13.8 [31,32]	0.157 [26]	6.33	10	$7 \cdot 10^{-11}$	$13.4 \cdot 10^{-11}$ [19]	$1.9 \cdot 10^{-15}$ [33]
$LiNbO_3$ (e-wave: $\mathbf{k} \parallel X$, $\mathbf{E} \parallel Z$)	14.7 [31,32]		4.74	7	$2 \cdot 10^{-11}$	$4.3 \cdot 10^{-11}$ [19]	$0.91 \cdot 10^{-15}$ [35]
NaCl	4.9 [21,36]	0.40 [37,38]	2.16	0.3	$-8 \cdot 10^{-13}$	—	$1.8 \cdot 10^{-15}$[39]
KCl	4.3 [26]	0.37 [37,40]	1.80	0.3	$-7 \cdot 10^{-13}$	—	$0.94 \cdot 10^{-15}$ [39]

Note * wave vector

3 orders of magnitude larger than in IR) due to the large value of the vibrational part of the linear refractive index and a greater effective frequency than in the considered isotropic crystals. Table 1 shows that the experimental values of n_2 for lithium niobate in the THz range correlate quite well with the theoretical estimates.

To justify further deductions, let us show that expression (2), obtained by iteration from (1), is equivalent to the exact solution of system (1) given in [12] for non-resonant quasi-monochromatic radiation. For this purpose, we will assume that the electric field of the quasi-monochromatic THz pulse is described by the expression

$$E = \frac{1}{2}\varepsilon_\omega(t)e^{i\omega t} + c.c., \tag{11}$$

where $\varepsilon_\omega(t)$ — the amplitude of the electric field of the THz pulse at the frequency ω. In this case, the nonlinear cubic polarization response can be represented as

$$P_{nl} = \frac{1}{2}\left(P_\omega^{nl}(t)e^{i\omega t} + c.c. + P_{3\omega}^{nl}(t)e^{i3\omega t} + c.c.\right), \tag{12}$$

where $P_\omega^{nl}(t)$ — amplitude of nonlinear cubic polarization response at frequency ω; $P_{3\omega}^{nl}(t)$ — amplitude of nonlinear cubic polarization response at frequency 3ω. Neglecting absorption and the time dependence of the THz electric field amplitude, let us substitute (11) and (12) in (2). Thus, we obtain an expression for the amplitude of the non-resonant nonlinear cubic polarization response (2) at the frequency ω

$$P_\omega^{nl} = \frac{3}{4}\chi_\omega^{(3)}|\varepsilon_\omega|^2\varepsilon_\omega, \tag{13}$$

where

$$\chi_\omega^{(3)} = \chi^{(3)} + \frac{2}{3}\chi^{(3d)}\frac{\omega^2}{\omega_0^2},$$

or

$$\chi_\omega^{(3)} = \frac{\chi_{\text{lin}}\alpha^2}{\omega_0^6}\left[\frac{2a^2}{\omega_0^2}\left(1 + \frac{16}{3}\frac{\omega^2}{\omega_0^2}\right) - b\left(1 + 4\frac{\omega^2}{\omega_0^2}\right)\right]. \tag{14}$$

On the other hand, according to [12], the cubic nonlinear polarization of the medium can be represented as

$$P_\omega^{nl} = \frac{3}{4}\chi_\omega^{(3)}|\varepsilon_\omega|^2\varepsilon_\omega,$$

$$\chi_\omega^{(3')} = \frac{1}{3}\frac{qN\alpha^3}{(\omega_0^2 - \omega^2 + i\gamma\omega)^3}\frac{1}{(\omega_0^2 - \omega^2 - i\gamma\omega)} \times \left[2a^2\frac{3\omega_0^2 - 8\omega^2 + 4i\gamma\omega}{\omega_0^2(\omega_0^2 - 4\omega^2 + 2i\gamma\omega)} - 3b\right]. \tag{15}$$

By neglecting the absorption in (15) and expanding this expression in a Taylor series by the small parameter ω/ω_0 (assuming $\omega_0 \gg \omega$), we obtain

$$\chi_\omega^{(3')} = \frac{\chi_{\text{lin}}\alpha^2}{\omega_0^6}\left[\frac{2a^2}{\omega_0^2}\left(1 + \frac{16}{3}\frac{\omega^2}{\omega_0^2}\right) - b\left(1 + 4\frac{\omega^2}{\omega_0^2}\right)\right]. \tag{16}$$

It is easy to see that expression (16) obtained from the exact solution of system (1) is identical to formula (14) obtained from (1) using the iteration method, It means that the two approaches are equivalent in the case under consideration.

Nonlinear vibrational response settling time in the terahertz radiation field

The vibrational part of the nonlinear cubic polarization response (2) can also be represented as a system

$$P_{nl} = \chi_{nl}E, \tag{17}$$

$$\tau_{disp}^2 \frac{\partial^2 \chi_{nl}}{\partial t^2} + \tau_{abs} \frac{\partial \chi_{nl}}{\partial t} + \chi_{nl} = \chi E^2,$$

where τ_{disp}, τ_{abs}, and χ are some time-independent parameters (to be defined below), since its solution by iteration method is equivalent to (2)

$$P_{nl} = \chi E^3 - 2\tau_{abs}\chi E^2 \frac{\partial E}{\partial t} - \chi(\tau_{abs}^2 + \tau_{disp}^2) \times E \left(\frac{\partial E}{\partial t}\right)^2 - 2\chi(\tau_{abs}^2 + \tau_{disp}^2) E^2 \frac{\partial^2 E}{\partial t^2}. \quad (18)$$

From this, it is easy to determine that $\chi = \chi^{(3)}$ and

$$\tau_{abs} = \frac{\gamma}{\omega_0^2} \frac{8a^2 - 3b\omega_0^2}{2a^2 - b\omega_0^2}, \quad (19)$$

$$\tau_{disp} = \sqrt{\frac{1}{\omega_0^2} \frac{8a^2 - 3b\omega_0^2}{2a^2 - b\omega_0^2} - \tau_{abs}^2} = \frac{1}{\omega_0} \sqrt{\frac{8a^2 - 3b\omega_0^2}{2a^2 - b\omega_0^2} \left(1 - \frac{8a^2 - 3b\omega_0^2}{2a^2 - b\omega_0^2}\right)}. \quad (20)$$

In the system of the form (17), the parameters τ_{disp} and τ_{abs} have the meaning of the inertia time constants for the vibrational nonlinearity mechanism, due to the dispersion and absorption of radiation in the medium, respectively. They characterize the rate of nonlinearity settling during in the interaction of the electric field of THz radiation with matter. From (20), we see that the dispersion and absorption inertia are interrelated. In the case $2a^2 \sim b\omega_0^2$ the inertia time constants tend to infinity. In such a case, according to (6), the nonlinear refractive index coefficient tends to zero. In other words, the infinite inertia time of the vibrational nonlinearity indicates the physical absence of this nonlinearity type in the medium.

Formulas (19), (20) should be used for materials, in which the quadratic and cubic contributions to the nonlinearity of the refractive index are comparable. For fluids in which, as shown in the previous section, the quadratic anharmonicity of local molecular oscillations dominates, (19) and (20) will be reduced

$$\tau_{abs}^a = \frac{4\gamma}{\omega_0^2}, \qquad \tau_{disp}^a = \frac{2}{\omega_0}\sqrt{1 - 4\frac{\gamma^2}{\omega_0^2}}. \quad (21)$$

In the opposite case, i.e., when the cubic anharmonicity of local molecular oscillations dominates, (19) and (20) will be simplified to the form

$$\tau_{abs}^b = \frac{3\gamma}{\omega_0^2} \qquad \tau_{disp}^b = \frac{\sqrt{3}}{\omega_0}\sqrt{1 - 3\frac{\gamma^2}{\omega_0^2}}. \quad (22)$$

Table 2 provides estimates of the inertia of the vibrational nonlinearity mechanism according to the formulas (19), (20) for the materials considered in Table 1. The values of the molecular oscillator damping coefficient γ values given in the last column of Table 2 were estimated from the half-width at half-height of the corresponding vibrational bonds. The table demonstrates that liquids have the shortest nonlinearity settling time while isotropic crystals — the longest, although the absorption coefficients of the former are much larger than those of the latter. The small inertia time in liquids is due to the small ratio γ/ω_0 which is a result of the location of the stretching vibrational bonds in the high-frequency area of the IR spectrum. It is worth noting that in all cases the dispersion inertia is several times greater than the absorption one. This is due to the fact that we consider the non-resonant interaction of radiation with matter, when the absorption is negligible.

Table 2. Results of numerical evaluation of inertia time constants related to absorption and dispersion of radiation in matter for vibrational nonlinearity mechanism in THz radiation field

Material	τ_{abs}, fs	τ_{disp}, fs	$\gamma/2\pi$, THz	γ/ω_0
H_2O	1	3	10.6 [22]	0.1
α-pinene $C_{10}H_{16}$	0.4	4	5.4 [24]	0.1
$LiNbO_3$ (o-wave: $\mathbf{k} \parallel X$, $\mathbf{E} \perp Z$)	10	20	3 [32]	0.2
$LiNbO_3$(e) (e-wave: $\mathbf{k} \parallel X$, $\mathbf{E} \perp Z$)	10	20	3 [32]	0.2
NaCl	20	50	1.28 [36]	0.3
KCl	30	50	1.28 [41]	0.3

The ratio of the nonlinear refractive index coefficient of vibrational nature to the vibrational nonlinear response settling time in the field of terahertz radiation

As mentioned above, the media for creating ultrafast THz photonics devices should have a maximum value of n_2 and a minimum value of the nonlinearity settling time. Therefore, to select materials in terms of their effectiveness for creating ultrafast THz photonics devices, it is reasonable to use the ratio n_2/τ, where $\tau \equiv \tau_{\max} = \max(\tau_{\text{disp}}, \tau_{\text{abs}})$. Thus, for more accurate calculations, it is necessary to calculate separately n_2, τ_{disp} and τ_{abs} via formulas (6), (19) and (20) respectively, and then calculate the ratio $n_2/\tau_{\max}$. However, as was shown above, the greatest vibrational nonlinearity have media with a dominant quadratic anharmonicity of local molecular oscillations. Moreover, the dispersion inertia time is usually greater than τ_{abs} in the considered non-resonant case. Therefore, instead of (19) and (20), only the second expression from (21) is acceptable for materials with large coefficient of thermal expansion and high-frequency vibrational bonds (i. e., primarily for liquids). Using these assumptions, the ratio n_2/τ can be simplified to

$$\frac{n_2}{\tau} = \frac{3\pi\chi_{lin}}{n_0}\frac{\alpha^2 a^2}{\omega_0^6\sqrt{\omega_0^2 - 4\gamma^2}}. \tag{23}$$

Based on the work [12], we have shown how the coefficients a and b are expressed through the known thermal and optical properties of matter. The α coefficient in the anharmonic oscillator model appears as $\alpha = q/m$. However, due to the fact that the effective charge and effective mass of the vibrational mode are quite complicated quantities for exact calculation, it is reasonable to express the parameter α through the non-resonant linear susceptibility of the vibrational nature similarly to what is done in [12]

$$\alpha = \frac{\omega_0^2}{4\pi qN}(n_{0,v} - 1). \tag{24}$$

Substituting (4), (7), (8) and (24) into (23), we obtain an expression for the ratio of the nonlinear refractive index coefficient of vibrational nature to the vibrational nonlinear response settling time, which can be estimated using the thermal, optical and spectral properties of matter well known from the reference literature

$$\frac{n_2}{\tau} = \frac{3}{64\pi^2 k_B^2}\frac{m^2 a_l^2}{q^2 N^2 n_0}\frac{\alpha_T^2\omega_0^6}{\sqrt{\omega_0^2 - 4\gamma^2}}(n_{0,v}^2 - 1)^3, \tag{25}$$

or, to simplify the constants,

$$\frac{n_2}{\tau} = 2.5\cdot 10^{29}\frac{m^2 a_l^2}{q^2 N^2 n_0}\frac{\alpha_T^2\omega_0^6}{\sqrt{\omega_0^2 - 4\gamma^2}}(n_{0,v}^2 - 1)^3, \tag{26}$$

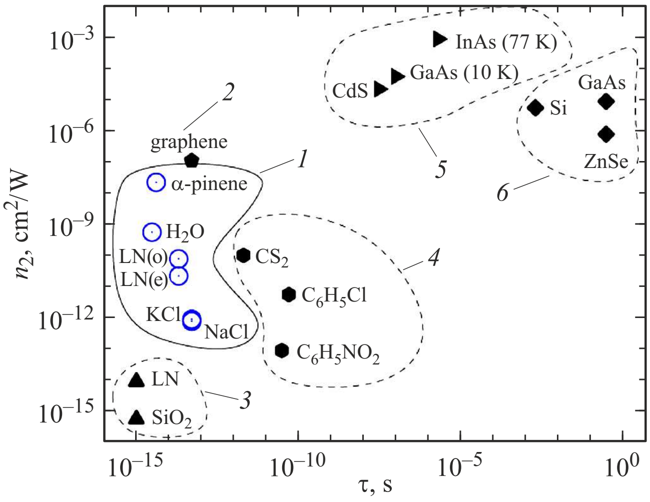

Diagram characterizing the ratio of the nonlinear refractive index coefficient to the nonlinear response settling time for different media and different types of nonlinearity: *1* — vibrational nonlinearity in the THz frequency range (results obtained in this paper), *2* — electronic nonlinearity in the THz frequency range [43], *3* — electronic nonlinearity in the visible frequency range [15,26], *4* — orientation nonlinearity [14], *5* — electronic nonlinearity in semiconductors [15], *6* — thermal nonlinearity [14].

and for the case of negligibly small absorption

$$\frac{n_2}{\tau} = 2.5\cdot 10^{29}\frac{m^2 a_l^2}{q^2 N^2 n_0}\alpha_T^2\omega_0^5(n_{0,v}^2 - 1)^3. \tag{27}$$

The formula (26) can be used as a characteristic parameter to evaluate the effectiveness of materials in terms of their application in ultrafast THz photonics devices. The greater the value we get from formula (26), the more efficient material we have. The formula (26) shows that the ratio n_2/τ for vibrational nature media is proportional to the square of the thermal expansion coefficient and approximately the fifth power of the frequency (in the case of media with low absorption) of the dominant stretching vibrational bond. All analytical formulas given in this work are written in the CGS system. To translate formula (26) into the SI system, it is necessary to use the ratio $n_2^{SI} = 4.2\cdot 10^{-3} n_2/n_0$ [12]

$$\frac{n_2^{SI}}{\tau} = 10^{27}\frac{m^2 a_l^2}{q^2 N^2 n_0^2}\frac{\alpha_T^2\omega_0^6}{\sqrt{\omega_0^2 - 4\gamma^2}}(n_{0,v}^2 - 1)^3. \tag{28}$$

Table 3 provides the absolute values of the ratio $n_2/\tau_{\max}$ obtained from the analytical data in Tables 1 and 2, as well as from formula (28) for the media considered in this paper. Table 3 shows that in the first approximation, it is quite acceptable to use the approximate formula (28) to estimate the nonlinearity efficiency of various materials in the THz range. Calculations have shown that the greatest efficiency in terms of the ratio n_2/τ is demonstrated by alpha-pinene, which has the highest nonlinear refractive index coefficient and the minimum inertia time. Liquid water is low-inertia as alpha-pinene, but has less n_2. The ratio n_2/τ in a crystal of lithium niobate is high enough for solids. Finally, vibrational nonlinearity of NaCl and KCl crystalls in the THz range is orders of magnitude less efficient in the other materials considered.

The Figure compares the ratio $n_2/\tau_{\max}$ for different nonlinearity mechanisms. The diagram clearly shows that the vibrational nonlinearity in the THz range is significantly superior to other types of nonlinearity in terms of efficiency. Thermal and electronic nonlinearity in semiconductors are very large, but too inertial, so they cannot be used to create radiation control devices. Electronic nonlinearity in the visible range is low inertia, but too small.

Due to recently increased interest in graphene structures, it is worth noting that the nonlinear refractive index coefficient of single-layer graphene in the infrared and THz spectral bands is about 10^{-7}–10^{-8} cm^2/W [42,43] with experimentally estimated inertia of the nonlinearity mechanism 10–100 fs [43,44]. In that case, for graphene $n_2/\tau_{\max} \sim 10^5$–$10^6$ cm^2/J. By the given ratio, graphene is comparable to alpha-pinene in the first approximation. However, for the giant nonlinearity graphene of structures in the THz range is responsible the diffuse collective motion of free electrons in the field of THz radiation [45]. Therefore, the formulas derived in this work are not applicable for the theoreti-

Table 3. The ratio of the nonlinear refractive index coefficient to the maximum nonlinear response settling time for the vibrational nonlinearity

Material	n_2, cm^2/W	$\tau_{\max}$, fs	$\lvert n_2/\tau_{\max}\rvert$, cm^2/J	$\lvert n_2/\tau\rvert$, cm^2/J
α-pinene $C_{10}H_{16}$	$2\cdot10^{-8}$	4	$5\cdot10^{6}$	$5\cdot10^{6}$
H_2O	$5\cdot10^{-10}$	3	$2\cdot10^{5}$	$2\cdot10^{5}$
$LiNbO_3$ (o-wave: $\mathbf{k}\parallel X$, $\mathbf{E}\parallel Z$)	$7\cdot10^{-11}$	20	$3.5\cdot10^{3}$	$4\cdot10^{3}$
$LiNbO_3$(e) (e-wave: $\mathbf{k}\parallel X$, $\mathbf{E}\parallel Z$)	$2\cdot10^{-11}$	20	$1.2\cdot10^{3}$	$1.4\cdot10^{3}$
NaCl	$-8\cdot10^{-13}$	50	20	7
KCl	$-7\cdot10^{-13}$	50	10	4

Table 4. The media properties used in this work to calculate n_2, τ_{disp}, τ_{abs}, and n_2/τ

Parameter	a_l, cm	n_0^*	n_{el}^*	ρ, g/cm^3	$m\cdot10^{24}$, g	$N\cdot10^{-22}$, cm^{-3}
H_2O	$2.8\cdot10^{-8}$ [47]	2.13 [48]	1.33	0.998 [49]	1.56	3.3
α-pinene $C_{10}H_{16}$	$6\cdot10^{-8}$ [50]	1.62 [18]	1.47 [51]	0.86 [20]	1.53	0.38
$LiNbO_3$(o)	$5.148\cdot10^{-8}$ [26]	6.63 [52]	2.21	4.63 [26]	7.6	1.9
$LiNbO_3$		5.1 [52]	2.14			
NaCl	$5.64\cdot10^{-8}$ [53]	2.45 [36]	1.53	2.17 [53]	23.2	2.2
KCl	$6.29\cdot10^{-8}$ [53]	2.1 [54]	1.47	1.99 [53]	31	1.6

Note. * Data are given for 1 THz for all substances except NaCl and KCl. In the case of these two materials — for 0.2 THz.

cal assessment of the graphene nonlinearity in the THz range.

Conclusion

In this work, on the basis of the theory of vibrational nonlinearity of materials analytical expressions for their nonlinear refractive index coefficient n_2 and inertia time constants in the field of pulsed THz radiation were obtained and analyzed. It is shown that the giant n_2 observed in a number of materials in the THz range is due to the significant contribution of the quadratic anharmonic local molecular oscillations to the macroscopic cubic polarization response of these substances to the THz radiation field. It is shown that the non-resonant settling time of the vibrational nonlinear response τ in the THz range is determined primarily by the radiation dispersion during interaction with the medium and is 1–100 fs. An analytical formula for the ratio n_2/τ was derived, which can be used as a characteristic parameter to evaluate the efficiency of materials in terms of their use in ultrafast THz photonics devices. It is shown that in the THz spectral range, the value of this ratio is determined by the squared matter thermal expansion coefficient and the fifth power of the frequency of its dominant stretching vibrational bond. This means that for THz photonics devices, materials with a large coefficient of thermal expansion and high-frequency stretching vibrational bonds are best suited. As a rule, such physical properties are typical for liquids. Estimates of the value of n_2/τ for a number of liquids and crystalline materials in the THz radiation field showed that vibrational nonlinearity in the THz spectral range is several times more effective than many other types of nonlinearity in various spectral areas. The liquid organic substance alpha-pinene has the highest value of the ratio n_2/τ among all the considered materials with different types of nonlinearity in different spectral ranges. For it $n_2/\tau\sim10^6$ cm^2/J.

Appendix. Parameters for calculations

Table 4 shows the matter parameters used in this work for analytical calculations. The effective mass of the vibrational bond for molecules of type A_xB_y (where x and y are the numbers of types A and B atoms in the molecule, respectively) was calculated using the formula for the reduced mass $m^{-1}=m_A^{-1}+m_B^{-1}$ where m_A is the mass of atom A; m_B is the mass of atom B [12]. This approach is based on the assumption that the stretching vibrations of two ions of a medium molecule act as the anharmonic oscillator in the material — for example, the O and H ions in a water molecule, or the C and H ions in an alpha-pinene molecule. The lithium niobate molecule is a more complex structure. It is difficult to figure out which groups of atoms make the main contribution to the nonlinear change in the refractive index. It can be supposed, that since the lithium and niobium ions are positively charged, and the oxygen ion — negatively charged, the common center of the Li and Nb cations in this molecule, in first approximation, oscillates with respect to the O anion (see also work [46]). From these considerations, the effective mass of the molecular oscillator in lithium niobate was calculated using the formula for the reduced mass of the three ions Li, Nb, and O as $m^{-1} = m_{\mathrm{Li}}^{-1} + m_{\mathrm{Nb}}^{-1} + m_{\mathrm{O}}^{-1}$. The number density of molecular oscillators was calculated using the formula $N = \rho/\Sigma x_i m_i$, where ρ is the density of matter, m_i is the mass of atom i in a molecule of matter, and x_i is the number of atoms i in a molecule of matter [12]. For the sake of simplicity, the value of the elementary charge was used as the effective charge of the vibrational mode $q = 4.8 \cdot 10^{-10}$ Fr [12].

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Conflict of interest

The authors declare that they have no conflicts of interest.

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